

# Thermal Degradation of Stabilized Rigid Poly (vinyl Chloride) Monitored by Microhardness Measurements

ANA GONZALEZ,\* JESUS MARTIN-GIL, and JOSE ANTONIO DE SAJA, *Laboratorio de Física del Estado Sólido, Facultad de Ciencias, Valladolid, Spain*, and RAMIRO RODRIGUEZ, *Rio Rodano S.A., Miranda de Ebro, Spain*

## Synopsis

Microhardness testing is shown to be a simple and useful complementary technique in the study of thermal degradation of rigid PVC stabilized with different amounts of an organotin compound. An interpretation of the microhardness observations is made in terms of reactions between the polymer and the stabilizer.

## INTRODUCTION

The thermal degradability of poly(vinyl chloride) (PVC) has been an important consideration in many of its numerous applications, and it has therefore been the subject of extensive testing and research. It is well known that temperatures above 100–120°C induce modifications in the chemical structure of this polymer as well as an undesirable loss of its mechanical and optical properties. In spite of the increasing number of publications in this field, the conclusive reasons for this process are still the subject of much speculation and many very important fundamental questions remain to be resolved.<sup>1</sup> It is generally admitted that the degradation of PVC may involve four separate reactions—dehydrochlorination with the formation of conjugated polyenes, oxidation, scission of chains, and crosslinking—and also that these four mechanisms operate somehow simultaneously with different degrees of importance.

Efforts to resolve this problem have led to the use of stabilizing additives. The ability of a certain number of metal-containing stabilizers to inhibit the HCl elimination is associated with the ability to replace labile Cl atoms of the chain by more thermally stable groups (Frye–Horst mechanism) and so to reduce the number of potential points of initiation of dehydrochlorination.<sup>2</sup>

Over the past few years, many types of laboratory tests, scattered throughout the literature, were attempted to demonstrate the effects of degradation and its evolution in PVC. These consisted of noting color changes, HCl evolution and general spectroscopic measurements. However, in the case of rigid PVC, because most of the damage in the degradation occurs close

\*Author for correspondence: Ana Gonzalez Facultad de Ciencias, Laboratorio de Física del Estado Sólido Valladolid, Spain.

to the surface we thought that a local estimation of its surface properties could be a complementary method in the study of this phenomenon. The selected technique has been a microindentation method of measuring of the surface hardness; microhardness testing used for about 75 years in metals<sup>3</sup> and nowadays in the study of certain properties of polymers<sup>4</sup> and ferroic compounds.<sup>5</sup> It is the aim of this work to check the suitability of this new method in the study of thermal degradation.

## EXPERIMENTAL

### Materials

The polymer used was a commercial stabilized PVC (Mirvil RB 8010, from Rio Rodano, Miranda de Ebro, Spain) produced by bulk polymerization at 69°C, with molecular weight 46,200, used in food packaging, rigid-pipe applications and in specialized electronic industry products. The stabilizer added was dioctyltin bis(2-ethylhexyl mercaptoacetate) [(C<sub>8</sub>H<sub>17</sub>)<sub>2</sub>Sn(SCH<sub>2</sub>—COOC<sub>8</sub>H<sub>17</sub>); X<sub>2</sub>SnY<sub>2</sub>] incorporated in the PVC by conventional hot milling techniques.

Three series of optically clear sheets of 2 mm thickness were prepared, by roll-milling at 150°C for 5 min and pressing at 160°C for 1 min at 10<sup>7</sup> N m<sup>-2</sup>, with 100 g PVC and (a) 0.7 g, (b) 1 g, and (c) 1.5 g of X<sub>2</sub>SnY<sub>2</sub>, respectively. The thermal histories of the three series of samples, prior to the degradation, were identical.

Systematic degradation studies were carried out by introducing the PVC sheets, measuring about 20 × 20 × 2 mm<sup>3</sup>, into a nitrogen-filled chamber held at 185°C, during controlled periods of time ranging from 10 to 140 min.

### Analytical Procedures

Vicker microhardness (MH<sub>v</sub>) measurements were carried out at room temperature by means of a microhardness tester combined with an optical Universal Zeiss microscope, using a diamond-pyramid indenter, in samples with different degrees of degradation. MH<sub>v</sub> values were calculated from the length of the diagonal (*d*) of the projected area of the indentation according the equation

$$MH_v = 1854.4 \times 10^7 \frac{P}{(d+D)^2} \text{ (N m}^{-2}\text{)}$$

where *P* is the load in ponds and *d* and *D* are the diagonals, respectively, corresponding to the plastic and the elastic contributions to the indentation (μm). The elastic recovery (from *D*) is calculated according to the method described in Ref. 6.

The MH<sub>v</sub> in polymers is strongly dependent on the applied load and on the time of application of this load. It is first necessary to determine the optimal conditions,<sup>7</sup> which in this case were a load of 60 ponds applied for 30 s. In each experiment it was noted that when the indenter load was removed, there was a large recovery of the depth of the indentation but

only a small recovery ( $\sim 3\%$ ) in the signal of the diagonals traced by the pyramid indenter. This latter dimension was the value used for  $d$  in the above equation.

In order to establish a relation between the  $MH_V$  values and other significant measurements of the degradation process, a series of complementary experiments was carried out in series (b) of PVC samples:

(i) The rate of incorporation of the mercaptoacetate groups in the PVC chains was monitored by IR techniques. These semiquantitative experiments are based on the fact that when an  $X_2SnY_2$  stabilizer is heated with PVC, the Y groups become so firmly bound to the polymer that they are not lost in repeated purification procedures.<sup>2</sup> Films suitable for infrared examination (0.2–0.3 mm thickness) were prepared by evaporation *in vacuo* of a tetrahydrofuran (THF) solution of each degraded sample. The separation of unreacted stabilizer was achieved by the following procedure: after dissolution in THF and filtration, the PVC was precipitated with methyl alcohol, removed by filtration, washed with methyl alcohol, and finally the filtrate was dissolved in THF and evaporated to dryness. The IR spectra were recorded on a Perkin-Elmer 580B computerized spectrometer. The appearance of a weak new band, observed at  $1730\text{ cm}^{-1}$  in the spectra after the stabilization treatment of PVC, proves the introduction of the Y groups in the chain. To improve the signal-to-noise ratio and also to expand the range of the detectable amounts of C=O bonds, we used averaging in the measurements of the spectra, and so every spectrum, in the range  $600\text{--}2000\text{ cm}^{-1}$ , was obtained as an average of 15 scans. In order to avoid any effect of thickness variation across the films we used the absorbance at  $630\text{ cm}^{-1}$  as an internal standard. Significant values were obtained for degradation times between 0 and 70 min; for longer times a noncontrolled oxidative degradation of the conjugated system, inherent in our experimental system of heating, leads to unreliable results.

(ii) The long polyene sequences formed during the degradation, responsible for the undesirable discoloration of the PVC, may take part in further reactions as cyclization and, in the case of solid samples, crosslinking.<sup>8</sup> As a consequence of this latter process, and when an interpenetrating network of crosslinked chains is formed, the PVC become partially insoluble in THF (gel point of the degradation process). The determination of the gel content for each time of degradation was carried out by weighing the gel remaining after all soluble components had been removed in the resin by Soxhlet extraction techniques.<sup>9</sup> In our experiment 1–2 g of polymer, of each degraded sheet, was placed in a cellulose thimble and extracted for 4 h with refluxing THF; the temperature in the thimble varied from  $63.5^\circ\text{C}$  to  $65.0^\circ\text{C}$ , a few degrees below the boiling point of THF. The insoluble material remaining was dried at  $50^\circ\text{C}$  to constant weight (3–4 h). From this value a relative gel content was defined in each degraded sheet.

## RESULTS AND DISCUSSION

The experimental results presented in Figure 1 show that when the samples of PVC resin were subjected to a thermal degradation process under a nitrogen environment:

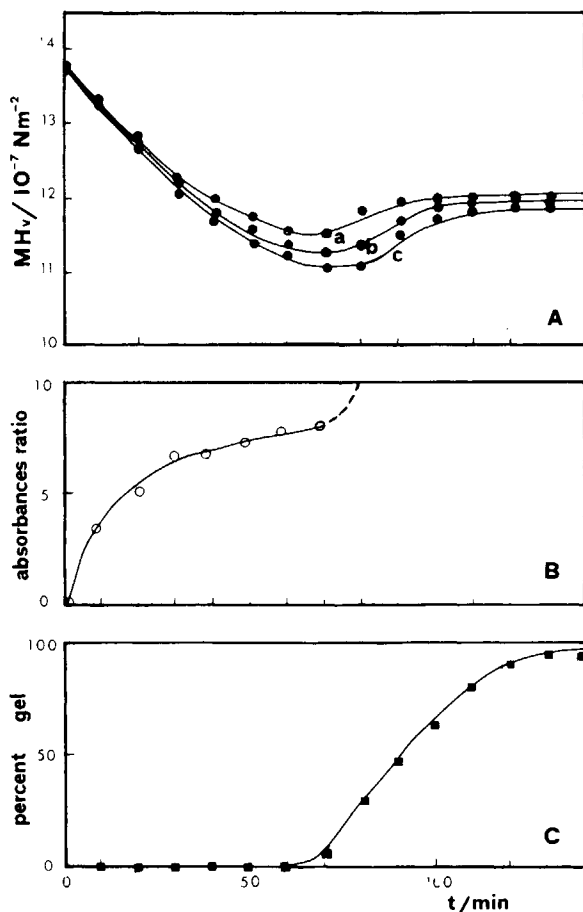


Fig. 1. (A) Variation of microhardness with the time of the thermal degradation ( $185^\circ\text{C}$ ,  $\text{N}_2$ ), in samples containing (g  $\text{X}_2\text{SnY}_2/100$  g resin): (A) 0.7; (b) 1; (c) 1.5. (B) Evolution of the ratio of IR absorbances at  $1730$  and  $630 \text{ cm}^{-1}$  (sample b). (C) Change of the percent of gel formed during degradation (sample b).

(A) Their superficial microhardness initially decreased, then passed through a minimum, and finally increased to reach a constant value. A gradual change in color from yellow (in the region of the minimum), yellow-brown to black (constant  $MH_v$  values) was perceived in the sheets. It is known that this discoloration depends on the conditions for removing the  $\text{HCl}$ ,<sup>10</sup> which is mainly a function of stabilizing compound and also of the physical state of the samples.

(B) The relative intensity of the  $1730 \text{ cm}^{-1}$  band, in the time range measured, increases gradually in such a way that the main incorporation of stabilizer groups in the chains take place prior to gelation.

(C) The content of gel in the sheets is measurable from 70 min of thermal degradation onwards. After this point the amount of gel formed increases linearly in the intervals measured. At the gel point the polymer shows a slightly yellow color that gradually deepens to black on processing.

The most outstanding conclusion of this preliminary investigation is that a microhardness study of the degraded material allows us to differentiate

two zones of distinct behavior in the curve  $MH_V$  vs. degradation time. According to the complementary measurements performed, the first zone is a consequence of the branching of voluminous Y groups to the PVC chains. This substitution reaction, as well as the subsequent inhibition in the HCl elimination, maintains the color but provokes a disorder and consequent disconnection between PVC chains, which leads to a decrease in the intermolecular cohesion and to a gradual loss of hardness. The second zone begins around the minimum of the curve, in a situation where the development of a crosslinked network is initiated; an increase in the microhardness up to a constant value, is the consequence of a gradual molecular structuration.

This discussion is consistent with the  $MH_V$  measurements obtained in sheets with different stabilizer amounts incorporated [Fig. 1(A) curves a, b, and c]. Thus curve c (higher concentration of  $X_2SnY_2$ ) corresponds to the series of samples in which the discoloration appears later and the  $MH_V$  reaches the lower values, with a minimum slightly shifted in relation to that of curves a and b. This is a result of a greater stabilizing action of the stabilizing compound in both substitution and HCl scavenging reactions. On the other hand as the crosslinking reactions are catalyzed by evolved HCl,<sup>10</sup> a higher concentration of  $X_2SnY_2$  implies a retardation in the rise of the  $MH_V$  values corresponding to the second zone of the curve.

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Received March 11, 1985

Accepted June 10, 1985